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The mechanisms controlling the growth of an oxide film during oxidation are subject to controversies at intermediate length scales (20-1000 nm) [1]. Relating rate-controlling mechanisms and resulting structural changes, which is essential to the understanding of oxidation processes, has proved challenging under these conditions.

Here, nickel particles are oxidized under 3.2 mbar of O_2 inside an environmental TEM (ETEM) equipped with a post-column filter [2]. Images, diffraction patterns and core-loss electron energy-loss spectra are acquired to monitor the structural and chemical evolution of Ni during oxidation, whilst increasing the temperature up to 600 °C.

Nucleation of NiO on Ni is observed to occur rapidly at room temperature before the introduction of O_2 in the environmental cell (in the vacuum of the microscope). It involves the formation of randomly orientated oxide domains of a few nanometres in size. These domains impinge and cover the particles surface. As the temperature increases under O_2, the NiO film grows and creates irregular structures composed of many crystallites. The reaction kinetics are inferred by EELS using different techniques analyzing changes in shapes of the Ni $L_{2,3}$ white lines [3]. The results indicate that the oxidation process is diffusion-controlled, similarly to results from the literature that were obtained at larger oxide thicknesses [1]. Pores are observed to form at the Ni/NiO interfaces, resulting in the loss of metal/oxide contact (Fig. 1). These observations illustrate that the outward diffusion of Ni^{2+} ions through NiO is the dominant mass transport mechanism under these conditions (in opposition to O_2/O^{2-} transport). Images also indicate that the NiO film might rupture in some regions, a process that should enable some inward diffusion of O_2 and therefore inward growth of NiO. An activation energy for Ni oxidation comparable to the ones found in the literature is determined from our EELS data.

By using ETEM, we are able to relate the structural and chemical changes occurring at the nanoscale during the oxidation of Ni particles with O_2 at high temperature, providing new insights into oxidation/corrosion processes.

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[3] Q. Jeangros*, et al.*, Acta Materialia, **58** (2010), p. 4578.
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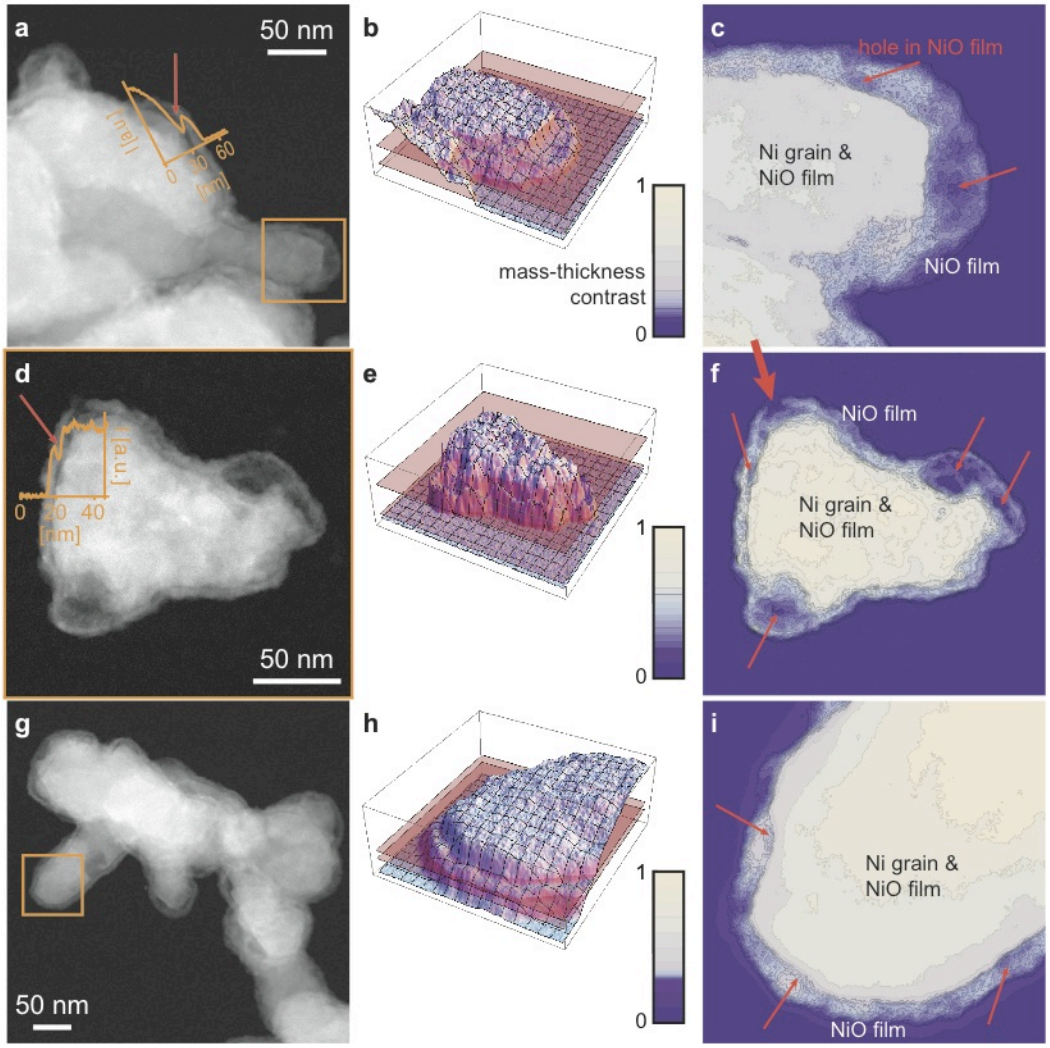

Figure 1: **a**, **d** and **g** STEM-HAADF images of Ni(O) particles at 300 °C under 3.2 mbar of O_2 along with intensity profiles. Arrows highlight a decrease in intensity at the NiO/Ni interfaces. Corresponding 3D histograms and contour plots are shown in **b**, **c**, **e**, **f**, **h** and **i**. The intensity scale of **c**, **f** and **i** has been adapted for each image to illustrate the differences in contrast located between the planes marked in red on the histograms **b**, **e** and **h**. Arrows indicate holes in the NiO film, while the larger one in **f** indicates what seems to be a fracture in the NiO film.